NAPHTHENE UPGRADING WITH PILLARED SYNTHETIC CLAY CATALYSTS

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ABSTRACT

Catalytic hydrotreatment of methylcyclohexane was investigated to model upgrading of coal-derived naphthenes. Nickel-substituted synthetic mica montmorillonite (NiSMM), alumina-pillared NiSMM, and zirconia-pillared NiSMM were prepared and tested for hydrocracking and hydroisomerization of methylcyclohexane. Infrared and thermal desorption studies of the pyridine-adsorbed catalysts indicated the presence of Lewis as well as Brønsted acid sites. Total acidity and surface area increased with pillaring of NiSMM with polyoxy aluminum and polyoxy zirconium cations. Most of the products were branched alkanes (isoparaffins). These compositions are highly desirable for environmentally acceptable transportation fuels. Furthermore, dehydrogenation was not a major pathway, as indicated by the minimal formation of aromatic hydrocarbons, coke, or other oligomeric materials. This paper describes the effect of various operating conditions, which included reaction temperature, contact time, hydrogen pressure, and catalyst on the product distribution.

INTRODUCTION

A growing need exists for new and improved catalysts to improve the overall economics of coal liquefaction. Coal-derived liquids are heavy, viscous, aromatic, hetero-compound-rich, and are very difficult and expensive to refine into transportation fuels. Natural clays were used as catalysts in petroleum cracking until replaced by more active and selective zeolites (1). Synthetic clays (SMM) containing a hydrogenation component were more active for hydrocracking and hydroisomerization (2-4). Synthetic clays such as nickel-substituted synthetic mica montmorillonite (NiSMM) were effective for cleaving carbon–carbon bonds and isomerizing the alkyl chains to give branched alkanes without extensive formation of aromatic hydrocarbons (5–8). These catalysts have also been found to be effective in hydrocracking and reforming of biomass materials to the isoparaffinic composition desired for transportation fuels (9–10). In the pillared clays, intercalation of hydroxylated or complexed metal cations maintains the clay layer structure after loss of water and generates large pore sizes. These structures are stable to 450° and 500°C. Pillared clays containing a hydrogenation component could be used for hydrogenation and hydrocracking processes.

The goal of this study was to develop an understanding of the hydrocracking and hydroisomerization of coal-derived cycloalkanes (naphthenes). Catalytic hydrotreating reactions of methylcyclohexane (MeCH) were conducted to evaluate the potential of synthetic and pillared synthetic clay catalysts for the upgrading of coal-derived liquids to an isoparaffinic product. The reactions of MeCH were carried out under several conditions to determine the effects of temperature, reaction time, and hydrogen pressure on the hydrocracking and hydroisomerization activity of NiSMM, alumina-pillared NiSMM, and zirconia-pillared NiSMM.

EXPERIMENTAL

Catalyst Preparation and Characterization

NiSMM was prepared by the procedure of Heinerman (11). Pillaring of NiSMM was carried out according to the procedure described earlier (12). The acidity of the solid acid catalysts was determined by pyridine adsorption and desorption studies. A small amount of sample (100 mg) was placed in a glass chamber attached to a vacuum pump, a gas inlet, and a gas outlet. The chamber was evacuated, and argon saturated with pyridine was introduced into the chamber until the weight increase ceased. At this stage, the chamber was evacuated until the physisorbed pyridine was removed, as indicated by the constant weight of the base absorbed sample. The amount of pyridine chemisorbed was used to determine total acidity of the catalyst. Surface area measurements were performed with Micromeritics AccuSorb 2100E static unit for nitrogen physisorption at 77K (BET method).

Catalytic Reactions

In a typical experiment, 0.5 g of MeCH and 0.25 g of the catalyst were placed in a tubing bomb (15-mL microreactor). The microreactor was evacuated, pressurized with desired amount of hydrogen, and placed in a rocking autoclave preheated to the desired temperature. At the end of the reaction period, the microreactor was cooled in a dry ice–acetone slurry, degassed, and opened. The

desired amount of the internal standard was added to the product slurry; the product slurry was transferred into a centrifugation tube by washing with methylene chloride; and the solid catalyst removed by centrifugation. Quantitative gas chromatography–flame ionization detection (GC–FID) analyses of the liquid samples were performed with a Hewlett-Packard 5890a gas chromatograph equipped with a Petrocol capillary column. The solid was dried in vacuum at 110°C for 3 hours. Since it was not found in the reaction products, octadecane was added as the internal standard. Alkane components were determined from the area percent ratio with respect to octadecane, assuming the same response factor.

RESULTS AND DISCUSSION

Total acidity of the NiSMM as measured by the amount of chemisorbed pyridine was found to be 0.84 mmol/g of catalyst, indicating the presence of acidic sites in the catalyst. These sites may be Lewis as well Brønsted acids. Pillaring the clay with polyoxyaluminum cations increased the total acidity to 1.02 mmol/g of catalyst. The increase in acidity is due to the additional acidic sites created by the dehydroxylation of the hydroxylated aluminum cations.

The surface area of the NiSMM was found to be 240 m^2/g. Pillaring the clay with polyoxy zirconium cations resulted in an increase in the surface area (274 m^2/g). The increase in surface area may be due to the micropores created by the dehydroxylation of the intercalated hydroxylated metal cations (pillars).

The results from the catalytic hydrocracking/hydroisomerization reactions of MeCH are given in Tables 1 and 2. In all these tests, conversion to liquid and gas products was 100%, and no coke or insoluble materials were detected on the recovered catalyst.

Temperature effects

A reaction of MeCH was carried out with alumina-pillared NiSMM at 350°C for 30 min in the presence of 1000 psi of initial hydrogen pressure. This reaction gave only 29% conversion of MeCH to products. The yields of liquid and gas products were 23% and 6% respectively. A reaction at 400°C gave considerably higher conversion (93%) of MeCH to liquid (72%) and gas (21%) products. There is therefore a large temperature effect and this experiment established that 400°C is a more appropriate temperature. Subsequent reactions were performed at 400°C.

The reaction products were a complex mixture of hundreds of components formed as result of the extensive rearrangements or isomerization of the primary cracked products. The major products from higher-temperature reactions were the desired isoparaffins (mono-, di-, and trimethylalkanes) with lower amounts of *n*-alkanes. The amount of aromatic hydrocarbons was insignificant.

Pressure effects

Reactions of MeCH were conducted under different initial hydrogen pressures to determine the effect on product yields and distribution. The reaction of MeCH with NiSMM at 400°C for 90 min in the presence of 1000 psi of initial hydrogen pressure gave almost complete conversion of the substrate to liquid (41%) and gas (58%) products. The reaction at 500 psi resulted in significant improvement in the yield of liquid products (72%), and gas yield was significantly lower (25%), owing to lower hydrocracking of MeCH and rearrangement products at the lower pressure. Pillared clay catalysts exhibited the same effect. The reaction of MeCH with alumina-pillared NiSMM (AlPNiSMM) at 400°C for 90 min in the presence of 200 psi of hydrogen (initial) gas only 36% conversion of the substrate to liquid (25%) and gas (11%) products. Increasing the hydrogen pressure to 500 psi resulted in substantial increase in the conversion of MeCH (90%) to give 68% yield of liquid products and 22% of gas products. The reaction with 1000 psi initial hydrogen pressure gave significantly high conversion of MeCH (99%), but the yield of liquid products was significantly lower (42%) with the remaining gas. The reaction of zirconia-pillared NiSMM (ZrPNiSMM) with MeCH at 400°C for 90 min in 500 psi (initial) hydrogen pressure gave 98% conversion to liquid product (68%) and gas product (30%). However, similar reaction with 1000 psi hydrogen pressure gave significantly lower amounts of liquid products and high gas yield (Table 1). Thus there is a large pressure effect on conversion of MeCH and also a large pressure effect on gas yield.

Reaction Time

The effect of reaction time on the product yields and product distribution was investigated with AlPNiSMM. The 30-min reaction gave 93% conversion of MeCH to products; the yields of liquid and gas products were 72% and 21% respectively. The reaction for 90 min resulted in almost complete conversion of MeCH to give a liquid product yield of 42%. The remaining substrate was converted into gaseous products. After 180 min, MeCH was completely converted into liquid (21%) and gaseous (79%) products. The effect of time was also studied by comparing the reactions of MeCH with AlPNiSMM for 30 and 90 minutes at 400°C in the presence of 200 psi of initial

hydrogen pressure. These reactions gave similar conversions of MeCH to volatile products (Table 1). The liquid product yield was somewhat higher for the 30-min reaction than for the 90-min reaction. Thus, over a longer period of time, primary cracked products are further cracked to form undesirable gaseous components, and a shorter reaction time favors liquid isoparaffinic products.

Selectivity

A comparison of the conversions obtained with the three catalysts at 500 and 1000 psi at 400°C indicate that there is no difference in activity. There is also no difference in the selectivity for total liquid product at 500 psi. At 1000 psi, the ZrPNiSMM appeared to give a somewhat better liquid yield (54%) than the NiSMM and AlPNiSMM.

Further information on the selectivity for hydrocracking and hydroisomerization reaction of the MeCH can be gained from comparison of the cyclic and isoparaffinic components in the products (Table 2). The reaction of MeCH with AlPNiSMM in 200 psi hydrogen gave larger amounts of dimethylcyclopentane (DMCP), indicating that hydrocracking is incomplete at lower hydrogen concentrations. The formation of four DMCP isomers (1,1-DMCP, *trans*-1,2-DMCP, *cis*-1,3-DMCP, and *trans*-1,3-DMCP) indicates that carbonium ions form initially on all carbons of the MeCH ring and rapidly rearrange via protonated cyclopropane (actually bicyclohexane) intermediates to the isomeric DMCPs.

The products at 500 psi with the three catalysts are mainly the isoparaffins. Thus, at higher pressures, cracking of the DMCP rearrangement products as well as the MeCH via carbonium ion intermediates increases, giving branched C_7 isomers and subsequently other isoparaffins. The ZrPNiSMM appears to be the most efficient catalyst for the ring hydrocracking reaction. This result is consistent with the higher acidity of this pillared catalyst. Previous work demonstrated that there is no difference in the three catalysts with respect to shape selectivity (9); hence, the effects seen here are likely the result of the acidity effects. The amounts of aromatic hydrocarbons were found to be minimal with all the catalysts, so dehydrogenation is not a major reaction of the MeCH.

The AlPNiSMM gives a quite different distribution of products from those of the other two catalysts. Since the *n*-heptane yield is high, the initial carbonium ion reaction may favor the rearrangement of 2-methylcyclohexylcarbonium ion to 2-ethylcyclopentylcarbonium ion, which cracks to *n*-heptane rather than branched heptanes. Ethylcyclopentane is one of the larger components in the products from this reaction. The lowered content of branched alkanes increased the DMCP:BA ratio. Thus the acidic AlPNiSMM is also efficient at hydrocracking but different initial rearrangements lead to different products.

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Table 1. Catalytic Reactions of Methylcyclohexane[a]

| Catalyst | Time, min | Temp, °C | Hydrogen, psig | Conversion, % | Products, % | |
					Liquid	Gas
NiSMM[b]	90	400	500	97	72	25
NiSMM	90	400	1000	99	41	58
AlPNiSMM[c]	30	350	1000	29	23	6
AlPNiSMM	30	400	1000	93	72	21
AlPNiSMM	30	400	200	37	28	9
AlPNiSMM	90	400	500	90	68	22
AlPNiSMM	90	400	200	36	25	11
AlPNiSMM	90	400	1000	99	42	57
AlPNiSMM	180	400	1000	100	21	79
ZrPNiSMM[d]	90	400	500	98	68	30
ZrPNiSMM	90	400	1000	99	54	45

[a] Substrate = methylcyclohexane; catalyst:substrate ratio = 0.5.
[b] Nickel-substituted synthetic mica montmorillonite.
[c] Alumina-pillared NiSMM.
[d] Zirconia-pillared NiSMM.

Table 2. Products from Reactions of Methylcyclohexane[a]

Catalyst	Hydrogen, psig	$\frac{BA^b}{nA^d}$	$\frac{DMCP}{BA}$	$\frac{OCA^c}{BA}$	$\frac{i\text{-}C_4}{n\text{-}C_4}$	$\frac{i\text{-}C_5}{n\text{-}C_5}$	$\frac{i\text{-}C_6}{n\text{-}C_6}$	$\frac{i\text{-}C_7}{n\text{-}C_7}$
NiSMM	500	3.2	0.2	0.2	2.2	5.1	5.7	3.1
ZrPNiSMM	500	2.7	0.1	0.1	2.1	4.3	5.2	4.2
AlPNiSMM	500	1.9	0.6	0.2	2.6	6.6	7.5	0.7
AlPNiSMM	200	4.9	6.7	2.3	2.3	7.9	10.6	12.4
AlPNiSMM	1000	3.3	0.6	0.3	2.5	6.6	8.4	2.6

[a] Reaction temperature = 400°C; reaction time = 90 min; catalyst:substrate ratio = 0.5.
[b] Branched alkanes.
[c] Cycloalkanes other than DMCP.
[d] Normal alkanes.